Chemical Engineering Dissertation Defense

Engineering Polymer Networks Using Stimuli-Responsive Nanoparticles

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Abstract

Stimuli-responsive polymer networks are adaptive materials that can change their structure, dynamics, mechanical properties, or chemical functions in response to external triggers. Although dynamic polymer networks have enabled advances in self-healing, stress relaxation, reprocessing, and controlled release, a persistent challenge is the trade-off between mechanical robustness and dynamic response. Networks that heal or relax rapidly often require high chain mobility and weak reversible interactions, whereas networks with high glass transition temperature and high modulus require restricted chain motion and stable junctions. This dissertation addresses this challenge by using stimuli-responsive nanoparticles as tunable building blocks for polymer network engineering. First, mechanically robust, self-healing polymer nanocomposites are developed using surface-functionalized gold nanoparticles as tailorable nanoparticle-based bonds. Carboxylic acid-functionalized nanoparticles form complementary hydrogen-bonding interactions with poly(N, N-dimethylacrylamide), allowing the nanoparticles to act as multivalent dynamic crosslinking junctions. Polymer–nanoparticle interfacial interactions are systematically tuned to control glass transition temperature, modulus, stress relaxation, self-healing behavior, and reversible assembly–disassembly by varying nanoparticle size, ligand density, nanoparticle concentration, and moisture content. Second, solid-state nuclear magnetic resonance spectroscopy is used to probe molecular-level hydrogen-bonding interactions and water dynamics in polymer nanocomposites. Because polymer–nanoparticle interfaces are buried within solid materials, this approach provides insight into interfacial interactions that are difficult to identify using bulk thermal or mechanical characterization alone. Third, design parameters of polymer networks with nanoparticle-based bonds are examined by varying polymer composition, polymer sequences, and ligand density. These studies show that polymer architecture and composition influence nanoparticle dispersion, interfacial binding, and glass transition temperature, establishing that both the nanoparticle surface and polymer matrix can be engineered to control nanocomposite properties. Finally, stimuli-responsive polyurethane nanocapsules are designed as programmable reservoirs for enzyme release. This strategy expands the role of nanoparticles from dynamic interfacial junctions to controlled-release components that introduce chemical function on demand. Taken together, this dissertation establishes stimuli-responsive nanoparticles as active and modular components for designing polymer networks with tunable mechanics, dynamic behavior, and controlled functional response.

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